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ABSTRACT

Composition for ceramics based on yttrium oxide containing titanium oxide.
This composition can be sintered to give a ceramic which is especially useful in the field of metallurgy.

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COMPOSITION
CASE,

COMPLETE SPECIFICATION

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COMPOSITION FOR CERAMICS AND PROCESSES FOR OBTAINING IT

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COMPOSITION FOR CERAMICS AND PROCESSES FOR OBTAINING IT

The present invention relates to a composition intended for the manufacture of ceramics. It also relates to processes for obtaining it and to
5 its use in the manufacture of sintered ceramic bodies.

Use of yttrium oxide by itself as a powder for ceramics does not make it possible to obtain a satisfactory ceramic because granular growth takes place too rapidly during densification. The material
10 must then be sintered at a very high temperature, generally above 1700°C. Without the aid of an external pressure, supplied, for example, by sintering under load or by an isostatic compacting with heating, the density remains limited by the intragranular porosity
15 at about 95% of the theoretical density. This residual porosity and the grain size are detrimental to the properties, especially mechanical ones.

The problem which arises is to accelerate the densification process relative to that of the granular
20 growth. It would then be possible to obtain ceramics which have high densities at a lower temperature, final densities closer to the theoretical density and an improved microstructure.

The objective of the invention is therefore
25 to find a formulation which promotes the sinterability of the yttrium oxide powder.

There has now been found, and this is what

forms the subject of the present invention, a composition based on yttrium oxide, intended for the preparation of a sintered ceramic body, characterised in that it comprises yttrium oxide and at least one
5 titanium oxide, or precursors of the said oxides.

A precursor of yttrium oxide and of titanium oxide means any yttrium or titanium compound (inorganic or organic salts, hydroxides, and the like) capable of producing an oxide phase under the conditions of
10 manufacture of the sintered ceramic body.

Titanium oxide means titanium oxide TiO_2 and/or a mixed Ti-Y oxide such as Y_2TiO_5 and/or $\text{Y}_2\text{Ti}_2\text{O}_7$.

In accordance with the present invention, it has been found that the presence of the titanium ion
15 during the sintering of yttrium oxide facilitates and increases the densification of yttrium oxide at a given sintering temperature.

In other words, it is possible according to the invention to obtain a ceramic with a given
20 densification at a sintering temperature which is lower than the sintering temperature of a powder containing only yttrium oxide.

The proportion of the titanium ions, expressed at TiO_2 , and yttrium ions, expressed as Y_2O_3 ,
25 may vary within wide limits. However, it is appropriate to use them in the following proportions:

- from 0.01 to 20% by weight of TiO_2
- from 80 to 99.99% by weight of Y_2O_3 .

A preferred composition is the following:

- from 0.02 to 10% by weight of TiO_2
- from 90 to 99.98% by weight of Y_2O_3 .

5 The composition which is the subject of the present invention is intended for the formation of the sintered ceramic body. It can assume a number of forms which are essentially related to their method of preparation which will be detailed below.

10 This composition may be all oxide, that is to say it may contain yttrium oxide and titanium oxide in the form of a single oxide, optionally of a mixed oxide Y_2TiO_5 , $\text{Y}_2\text{Ti}_2\text{O}_7$.

It may be in the form of a mixture of yttrium oxide and of a precursor of titanium oxide.

15 It is also possible for both yttrium and titanium to be in the form of a precursor in the case where a coprecipitate is used.

In all cases the oxide precursor will be converted into its corresponding oxide either during a precalcination stage if desired or during the sintering
20 of the composition in order to obtain the sintered ceramic body.

As mentioned above, the composition for ceramics of the invention may be prepared in various
25 ways.

A first alternative form of the invention consists of a "chamotte production" technique. An intimate mixture of yttrium oxide with at least one

titanium oxide is produced, optionally followed by drying.

The yttrium oxide used in the invention is a product which is known and described in the literature.

5 It can be prepared especially by heating in air, between 400°C and 1000°C, yttrium hydroxide or some oxygen-containing salts such as nitrates, sulphates, carbonates, oxalates and acetates (cf. Paul Pascal - Nouveau Traité de Chimie Minérale [New
10 Treatise on Inorganic Chemistry], Volume VII).

It is preferable that the yttrium oxide used should be of high purity, preferably higher than 99%.

As for titanium oxide, that used may be titanium monoxide, titanium sesquioxide or titanium
15 dioxide in anatase or rutile form.

It is also possible to introduce the titanium ions in the form of a mixed yttrium titanium oxide and especially Y_2TiO_5 and $Y_2Ti_2O_7$. These are obtained, for example, by making a chamotte from a mixture of
20 titanium and yttrium oxides in appropriate proportions at approximately 1300°C.

A mixture of the abovementioned oxides may also be used.

The proportion of the various oxides used is
25 such that the weight percentages as defined above are present.

If necessary, the various oxide powders are broken up so as not to present hard agglomerates. It is

- 5 -

desirable that their particle size range should be such that their mean diameter is smaller than or equal to 1 μm , the particle size analysis being carried out with the aid of the Sedigraph 5000 D instrument, which measures the
5 distribution of the suspended particles.

The mean diameter is defined as being a diameter such that 50% by weight of the particles have a diameter greater than or smaller than the mean diameter.

In most cases, in order to obtain powders of the
10 desired particle size, milling is carried out, which may be performed wet or dry.

Air jet milling can be used but, in most cases, the milling is conducted conventionally dry or in suspension in the presence or absence of additives which are usual in
15 these techniques: milling agents and dispersants.

The milling of the oxide powders is preferably performed in suspension in water or in an organic liquid such as alcohols, for example methanol, ethanol, n-propanol or isopropanol, or aldehydes or ketones such as, for
20 example, benzaldehyde and, optionally, in the presence of a dispersing agent such as, for example, sodium hexametaphosphate, sodium silicate, triethanolamine, ammonium polyacrylates, glycols such as propylene glycol, diethylene glycol, triethylene glycol, and the like.

25 At the end of this milling operation a

mixture is obtained which may contain from 40 to 80% of water or organic liquid. It is then desirable to remove it by drying.

The drying is carried out at a temperature which depends on the liquid to be removed and which is in most cases between 20 and 400°C but preferably between 20 and 150°C. This operation can be carried out in air or under reduced pressure, for example between 1 and 100 mm of mercury (133.322 Pa and 13332.2 Pa).

It may be performed especially using the spraying technique, that is to say by spraying into a stream of hot air whose temperature is chosen in the abovementioned range.

The heating time depends on the quantity of liquid to be removed and on the technique employed. It can therefore vary within wide limits, for example between 15 minutes and 48 hours.

Another embodiment of the invention consists in preparing the composition for ceramics according to a coprecipitation process which consists:

- a) in performing a coprecipitation of a compound of yttrium and of titanium from a solution of soluble salts of the abovementioned elements,
- b) in isolating the coprecipitate obtained,
- c) in then optionally calcining it.

In the first stage of the process of the invention, yttrium and titanium are coprecipitated.

The starting solutions of soluble salts may

be aqueous or organic solutions of inorganic or organometallic compounds.

With regard to the organic solvent, one which is miscible with water is chosen, preferably an
5 aliphatic alcohol containing from 1 to 4 carbon atoms, or a glycol such as, for example, ethylene glycol or diethylene glycol.

The solutions of soluble yttrium salts which are employed to start with are preferably yttrium
10 nitrate, chloride and/or sulphate solutions.

The yttrium salt is chosen so that it does not contain any impurities which can recur in the calcined product. It may be advantageous to make use of an yttrium salt of a purity which is higher than 99%.

15 The concentration of the yttrium salt in solution is not a critical factor according to the invention and it can vary within wide limits; a concentration of between 0.2 and 4 moles per litre is preferred.

20 With regard to the titanium salts, a nonlimiting list of compounds which can be employed is given below: titanium chloride, titanium oxychloride, a titanium alcoholate derived from an aliphatic alcohol containing from 1 to 4 carbon atoms such as, for
25 example, titanium tetramethylate, tetraethylate, tetra-n-propylate, tetraisopropylate, tetra-n-butylate and tetraisobutylate. The titanium salt is preferably chosen to be of high purity, like the yttrium salt.

The concentration of the titanium salt in the solution is not critical and may also vary preferably between 0.002 and 0.04 moles per litre.

The various abovementioned compounds are
5 mixed in any order, the proportions being such that the weight proportions defined above are obtained.

Hydroxides, oxalates and carbonates may be mentioned especially as compounds of yttrium and titanium which may be precipitated.

10 The coprecipitation of the hydroxides may be performed by mixing a solution of the soluble salts with a basic solution.

The basic solution used may be especially an aqueous solution of aqueous ammonia or of sodium
15 hydroxide or potassium hydroxide. A solution of aqueous ammonia is preferably used. The normality of the basic solution used is not a critical factor according to the invention; it may vary within wide limits, but it will nevertheless be advantageously between 1 and 5 N,
20 preferably 2 to 3 N.

The proportion of the basic solution to the solution of soluble salts of yttrium and titanium must be such that the number of base equivalents is higher than or equal to the number of yttrium and titanium
25 equivalents. The pH of the reaction medium is not critical and may vary between 7 and approximately 14. It is advantageously between 9 and 12.

The temperature of the reaction medium is

generally preferably between 10 and 95°C.

A mixed coprecipitate of yttrium and titanium hydroxides is obtained.

Another method of precipitation may be especially the oxalic coprecipitation.

The solutions of yttrium and titanium salts comply with the abovementioned characteristics.

As for the precipitating agent, that used may be oxalic acid or its salts, preferably ammonium, in anhydrous or hydrated form.

It may be used in crystalline form or in the form of an aqueous solution.

In this case, the concentration, expressed as oxalic acid, may vary between 0.8 and 3 moles/litre, preferably 0.3 to 1 mole/litre.

The proportion of the oxalic solution to the solution of soluble yttrium and titanium salts is such that the number of oxalic equivalents is equal to or greater than the number of yttrium and titanium equivalents. An excess representing up to 50% of stoichiometry may be employed.

The coprecipitation is performed at a temperature of between 10 and 95°C and at a pH of 5.5 to 6.

A coprecipitate of yttrium and titanium oxalates is obtained.

The second stage of the process consists in isolating the coprecipitate from the suspension

obtained. This isolation may be performed by conventional liquid/solid separation techniques such as decanting, draining, filtering and/or centrifuging.

According to an alternative form of the
5 process of the invention, the isolated coprecipitate may then be washed with water.

The product obtained after isolation and optionally washing may then be dried under the conditions described above. The drying temperature is
10 preferably between 20 and 150°C; the drying time preferably varying between 15 minutes and 48 hours.

The dry product may then be calcined.

The calcination is generally performed at a temperature of between 400 and 600°C.

15 The calcination time may vary between 30 minutes and 24 hours, for example, and preferably between 1 and 13 hours.

The calcination time is related to the temperature and it is proportionally shorter the higher the calcination
20 temperature.

Another alternative form of embodiment of the invention consists in employing the technique of impregnating yttrium oxide with a solution of at least one titanium salt capable of decomposing to oxide when
25 heated, which will be called, simply, an oxide precursor.

The abovementioned soluble salts, converted into aqueous or organic solution as described above,

may be employed as oxide precursors.

The concentration of the oxide precursor solution depends on the solubility of the said precursor.

In practice, the impregnation may be carried out by
5 introducing a soluble titanium salt during the
disintegration of the yttrium oxide in an alcoholic medium,
for example by introducing an organometallic titanium
compound such as, for example, the tetrabutylate or the
tetraisopropylate, and by hydrolysing this organometallic
10 compound by adding water. The suspended oxide powders are
then dried as in the case of the chamotte production
technique. Drying and calcination may be conducted
according to the conditions given above.

The compositions of the invention which are
15 obtained by the various routes are intended for the
manufacture of ceramic bodies. Their particle size is
preferably such that their mean diameter is smaller than or
equal to approximately 1 μm , with a particle size
distribution which is as unimodal as possible.

20 The compositions described above are fabricated by
known processes such as uniaxial, isostatic pressing or
else by casting or injection.

The body is then baked so that it undergoes the
densification which is needed to form the sintered ceramic
25 body according to the invention.

Another subject of the present invention is

the sintered ceramic body which has a high density and comprises essentially approximately from 80 to 99.99% by weight of yttrium, expressed as yttrium oxide, and approximately from 0.01 to 20% by weight of titanium, expressed as TiO_2 .

The theoretical density of yttrium oxide is 5.031 g/cm^3 .

The sintered ceramic body obtained from the composition of the invention has a density of at least 4.50 g/cm^3 , which corresponds to a relative density representing 90% of the theoretical relative density determined as a function of the lattice parameters.

It is advantageous that the sintered ceramic body should have the following composition approximately of 90 to 99.98% by weight of yttrium oxide and from 0.02 to 10% by weight of titanium oxide.

The ceramic body obtained then has a density which is very close to the theoretical density, which is preferably situated above 4.78 g/cm^3 , which corresponds to a relative density representing from 95 to 100% of the theoretical relative density.

After fabrication, the body obtained is therefore sintered in the course of a heat cycle whose temperature ranges between room temperature and 1700°C , preferably between room temperature and 1550°C and the temperature is maintained when it reaches from 1300 to 1550°C over a period which depends on the temperature and the desired microstructure. The examples may be

referred to for further details on this temperature plateau.

It should be noted that very high densities are obtained at moderate sintering temperatures. A
5 decrease of 300 to 400°C in the sintering temperature is observed, relative to that needed to sinter yttrium oxide by itself.

Furthermore, the sintered ceramic body exhibits a very good microstructure without exaggerated
10 grain growth.

By way of illustration, reference may be made to Figures 1 and 2, which show photographs of various ceramics taken with the scanning electron microscope (with a magnification of 5000 and 10000 respectively).

15 Figure 1 shows the microstructure of a ceramic consisting of yttrium oxide by itself, sintered at 1500°C.

Figure 2 shows the microstructure of a powder containing 99% of Y_2O_3 and 1% of TiO_2 sintered at
20 1500°C. Reference will be made to Example 1 for further details on its preparation.

From the comparison between Figure 1 and Figure 2 it follows that the presence of the abovementioned sintering additives appreciably improves
25 the microstructure of the ceramic obtained.

As a result of their good properties, the compositions of the invention can be used especially as raw materials in the manufacture of ceramics, as

- 14 -

reinforcers for alumina and as milling media. They can also be used in the field of metallurgy, especially for the production of crucibles and filters for liquid metals.

The examples which follow illustrate the invention
5 without, however, limiting it.

The percentages which are given in the examples are expressed on a weight basis.

EXAMPLES 1 to 3

In this example, the composition of the invention
10 is prepared by mixing powdered yttrium oxide and titanium oxide.

The following powders are mixed in ethanol, introduced in a quantity which is equivalent to the charge, in a zircon ball mill (Attritor) rotating at 400
15 revolutions/minute:

- the yttrium oxide employed, marketed by Rhône-Poulenc, having a mean particle diameter of 3.4 μm , measured in the Sedigraph, and having a purity of 99.99% (luminophor grade)
- 20 - the anatase titanium oxide TiO_2 having a mean particle diameter of 8.5 μm and having a purity higher than 99%.

To begin with, 50 g of yttrium oxide are introduced into the mill and are milled for one hour in ethanol, used in a proportion of 60%.

25 Titanium oxide is then added in a suitable quantity defined in Table I and a combined milling is

performed for 30 minutes.

The ethanol and the water are removed by evaporation in an evaporator under a reduced pressure, produced by a water pump.

5 A composition is obtained in the form of powder, which is subjected to a screening operation, enabling agglomerates larger than 400 μ m in diameter to be removed.

10 It is then pelleted at a pressure of 150 MPa and subjected to the sintering operation.

The temperature is raised progressively at 20°C/min up to 1000°C and then at 3°C/min up to the sintering temperature of 1500°C; the said temperature is maintained for 3 hours.

15 The results obtained are listed in Table I.

TABLE I

	Example	1	2	3
20	% TiO ₂	1	3	10
	d	4.83	4.88	4.93
25	dr %	96%	97%	98%

In the said table, d denotes the relative density of the ceramic obtained, measured by Archimedes' technique using demineralised water as liquid, and dr is the

relative density expressed as a percentage of the theoretical density calculated on the assumption of a two-phase Y_2O_3 - Y_2TiO_5 mixture.

The ceramic obtained has a good microstructure.

- 5 It has grains which are substantially of the same shape and exhibits a uniform distribution of their size, which varies between 1 and 5 μm after sintering at 1500°C.

EXAMPLES 4 and 5

- In the examples which follow, a composition
10 containing yttrium oxide and titanium oxide is prepared by an impregnation technique.

 50 g of yttrium oxide are mixed with 50 cm^3 of ethanol. 0.425 g of titanium tetra-n-butylate are then added, corresponding to 0.2% of TiO_2 .

- 15 The whole is then subjected to a milling operation for 15 minutes in a zircon ball mill (Attritor) rotating at 200 revolutions/minute.

 10 cm^3 of distilled water are then added and the milling operation is continued for 1 hour 45 minutes.

- 20 The ethanol and the water are removed by evaporation in an evaporator under reduced pressure, produced by a water pump.

 A composition is obtained in the form of a powder, which is screened at 100 μm .

It is then pelleted at a pressure of 150 MPa and subjected to a sintering operation.

The temperature is raised progressively at 15°C/min up to 1100°C and then at 5°C/min up to the sintering temperature of 1500°C; the said temperature is maintained for 3 hours.

The results obtained are listed in Table II.

TABLE II

Example	4	5
% of TiO ₂	0.2	1
d	4.83	5.01
dr %	96.0%	99.5%

EXAMPLES 6 and 7

In this example the composition of the invention is prepared from yttrium oxide and Y₂Ti₂O₇.

The combined milling of Y₂O₃ and Y₂Ti₂O₇, which are introduced in the proportions defined in Table III, is carried out for 2 hours in ethanol in a zircon ball mill rotating at 200 revolutions/minute.

The ethanol and the water are removed by evaporation in an evaporator under reduced pressure,

produced by a water pump.

A powder is obtained and is screened at
100 μm .

It is then pelleted at a pressure of 150 MPa.

- 5 The sintering is carried out under the conditions of
Examples 4 and 5 (sintering temperature = 1500°C).

The results obtained are listed in Table III.

TABLE III

10	Example	6	7
	% of TiO_2	0.2	1
	d	4.79	5.02
15	dr %	95.2%	99.8%

CLAIMS

1. Composition for ceramics, based on yttrium oxide, characterised in that it comprises yttrium oxide and at least one titanium oxide, or
5 precursors of the said oxides.

2. Composition for ceramics according to claim 1, characterised in that the titanium oxide is TiO_2 and/or Y_2TiO_5 and/or $\text{Y}_2\text{Ti}_2\text{O}_7$.

3. Composition for ceramics according to
10 claim 1, characterised in that it comprises yttrium oxide and titanium oxide and/or a mixed yttrium-titanium oxide, yttrium oxide and a titanium oxide precursor, or yttrium oxide and titanium oxide, both in the form of oxide precursors.

15 4. Composition for ceramics according to claim 3, characterised in that the titanium oxide precursor is a titanium salt or a titanium alcoholate; the yttrium and titanium oxide precursors are a hydroxide, oxalic or carbonate coprecipitate.

20 5. Composition for ceramics according to claim 1, characterised in that it comprises:

- from 0.01 to 20% by weight of TiO_2
- from 80 to 99.99% by weight of Y_2O_3 .

25 6. Composition for ceramics according to claim 2, characterised in that it comprises:

- from 0.02 to 10% by weight of TiO_2
- from 90 to 99.98% by weight of Y_2O_3 .

7. Process for the preparation of the

composition for ceramics, described in one of claims 1 to 6, characterised in that it consists in intimately mixing yttrium oxide and at least one titanium oxide and optionally drying the mixture obtained.

5 8. Process according to claim 7, characterised in that the yttrium and titanium oxides have a purity which is higher than 99%.

 9. Process according to claim 7, characterised in that the oxide powders have a particle size such that the
10 mean diameter is smaller than or equal to 1 μm .

 10. Process according to one of claims 7 to 9, characterised in that the titanium oxide may be a titanium monoxide, a titanium sesquioxide, a titanium dioxide in anatase or rutile form, or a mixed oxide Y_2TiO_5 and/or
15 Y_2TiO_7 .

 11. Process according to one of claims 7 to 10, characterised in that the intimate mixture is produced by wet or dry milling.

 12. Process according to one of claims 7 to 11,
20 characterised in that the drying is carried out at a temperature of between 20 and 150°C.

 13. Process for the preparation of the composition for ceramics, described in one of claims 1 to 6, characterised in that it consists:

25 a) in performing a coprecipitation of yttrium and titanium compounds from a solution of soluble salts of the abovementioned elements,

- b) in isolating the coprecipitate obtained,
- c) in optionally calcining it.

14. Process according to claim 13,
characterised in that the solution of soluble yttrium
5 salt may be a nitrate, chloride and/or sulphate
solution.

15. Process according to one of claims 13
and 14, characterised in that the soluble titanium salt
may be titanium chloride, titanium oxychloride or a
10 titanium alcoholate derived from an aliphatic alcohol
containing from 1 to 4 carbon atoms.

16. Process according to one of claims 14
and 15, characterised in that the said salts are in
aqueous or organic solution.

15 17. Process according to one of claims 13 to
16, characterised in that the said elements are
coprecipitated in the form of hydroxides, oxalates or
carbonates.

18. Process according to claim 13,
20 characterised in that a coprecipitation of the
hydroxides is performed by mixing the solution of the
soluble salts of the said elements with a basic
solution.

19. Process according to claim 18,
25 characterised in that the pH of the reaction medium is
from 9 to 12.

20. Process according to claim 13,
characterised in that a coprecipitation of the oxalates

is performed by mixing the solution of the soluble salts of the said elements with oxalic acid or its salts.

21. Process according to claim 20,
5 characterised in that the precipitating agent is ammonium oxalate.

22. Process according to one of claims 20 and 21, characterised in that the pH of the reaction medium is 5.5 to 6.

10 23. Process according to one of claims 13 to 22, characterised in that the drying is performed at a temperature of between 20 and 150°C.

24. Process according to one of claims 13 to 23, characterised in that the calcination is performed
15 at a temperature of between 400 and 600°C.

25. Process for the preparation of the composition for ceramics, described in one of claims 1 to 6, characterised in that it consists in impregnating yttrium oxide with a solution of at least one titanium
20 salt and then optionally performing a drying and a calcining operation.

26. Process according to claim 25, characterised in that the titanium salt may be titanium chloride, titanium oxychloride or a titanium alcoholate
25 derived from an aliphatic alcohol containing from 1 to 4 carbon atoms.

27. Process according to claim 25, characterised in that the drying is performed at a

temperature of between 20° and 150°C and the calcination at a temperature of between 400 and 600°C.

28. Sintered ceramic body prepared from the composition described in one of claims 1 to 6,
5 characterised in that it comprises essentially approximately from 80 to 99.99% by weight of yttrium, expressed as Y_2O_3 , and approximately from 0.01 to 20% by weight of titanium, expressed as TiO_2 .

29. Sintered ceramic body according to claim
10 28, characterised in that it comprises essentially approximately from 90 to 99.98% by weight of yttrium, expressed as Y_2O_3 , and approximately from 0.02 to 10% by weight of titanium, expressed as TiO_2 .

30. Sintered ceramic body according to one
15 of claims 28 and 29, characterised in that it has a density higher than 4.50 g/cm³.

31. Sintered ceramic body according to claim
30, characterised in that it has a density higher than 4.78 g/cm³.

20 32. Sintered ceramic body according to one of claims 30 and 31, characterised in that the said density is obtained after sintering at a temperature of between 1300 and 1700°C.

33. A composition for ceramics according to claim 1, substantially as hereinbefore described and exemplified.

34. A process for the preparation of a composition for ceramics according to claim 1, substantially as hereinbefore described and exemplified.

35. A composition for ceramics according to claim 1, whenever prepared by a process claimed in a preceding claim.

36. A sintered ceramic body according to claim 28, substantially as hereinbefore described and exemplified.

Dated this the 10th day of May, 1991

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RHONE-POULENC CHIMIE

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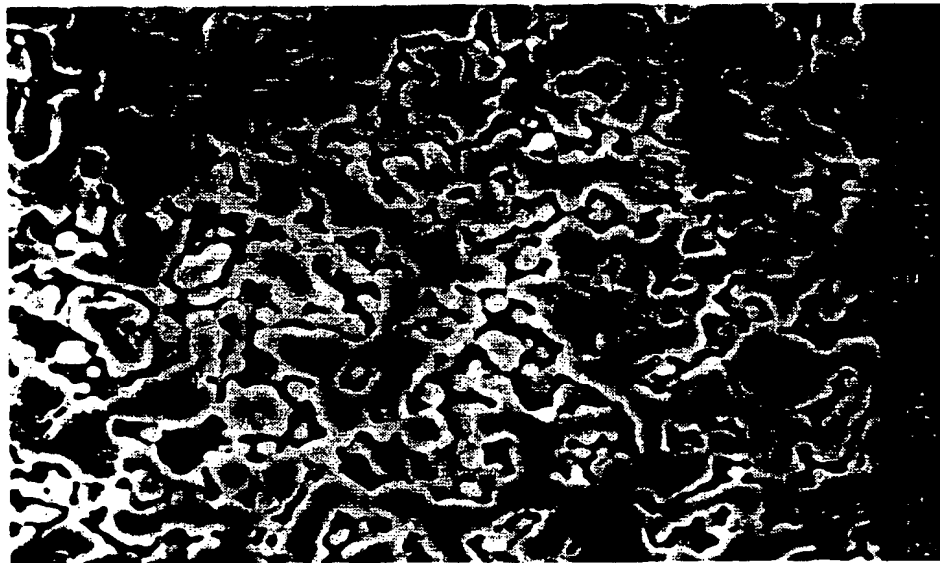


FIG. 1

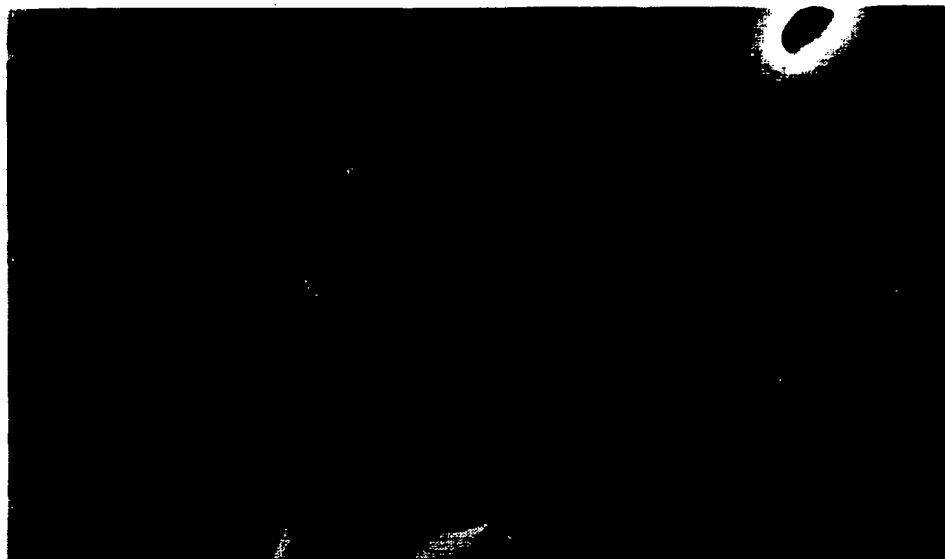


FIG. 2

F. R. KELLY & CO.